

**Atomization energies of SO and SO₂;
basis set extrapolation revisited**

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Abstract

The addition of tight functions to sulphur and extrapolation to the complete basis set limit are required to obtain accurate atomization energies. Six different extrapolation procedures are tried. The best atomization energies come from the series of basis sets that yield the most consistent results for all extrapolation techniques. In the variable α approach, α values larger than 4.5 or smaller than 3, appear to suggest that the extrapolation may not be reliable. It does not appear possible to determine a reliable basis set series using only the triple and quadruple zeta based sets. The scalar relativistic effects reduce the atomization of SO and SO₂ by 0.34 and 0.81 kcal/mol, respectively, and clearly must be accounted for if a highly accurate atomization energy is to be computed. The mag-

nitude of the core-valence (CV) contribution to the atomization is affected by missing diffuse valence functions. The CV contribution is much more stable if basis set superposition errors are accounted for. A similar study of SF, SF⁺, and SF₆ shows that the best family of basis sets varies with the nature of the S bonding.

I. INTRODUCTION

The calculation of accurate bond energies or atomization energies has many important applications. While there are several approaches to this problem, the common thread is the determination of the equilibrium geometries and calculation of the zero-point energies at a modest level of theory (such as density functional theory, DFT), the calculation of the bond energies using an accurate treatment of the electron correlation problem (such as the coupled cluster singles and doubles approach¹ with a perturbational estimate of the connected triples², CCSD(T)), and a correction to reach the basis set limit. The inclusion of relativistic effects and core-valence (CV) correlation are also required for some systems. The largest uncertainty in these procedures probably comes from the correction for basis set incompleteness, whether the G2 additive type correction³ is used or an extrapolation⁴⁻⁶ approach is used. No approach appears to be fail proof, for example, the usually reliable G2 approach does not work well for SiF_n, whereas basis set extrapolation works well for these systems⁷, while we have shown⁸ that basis set extrapolation, using the standard basis sets, does not work well for SO₂.

The (augmented-) correlation-consistent polarized-valence ((aug-) cc-pV) sets, which were developed by Dunning and co-workers⁹⁻¹², have been used extensively in studies that include basis set extrapolation. Extrapolation using the triple zeta (TZ), quadruple zeta (QZ), and quintuple zeta (5Z) sets has proven to yield accurate bond energies in most cases. However, Bauschlicher and Partridge⁸ showed that

missing tight functions on sulphur resulted in an inaccurate extrapolation for the atomization energy of SO_2 . That is, if a family of basis sets is deficient in some systematic way, extrapolation will not overcome the deficiency and will therefore not yield reliable results. This problem is not unique to SO_2 , we have recently found this also applies to SF_n ¹³ and Martin^{14,15} found it for several additional second-row compounds.

In their study, Bauschlicher and Partridge⁸ showed that adding a tight d function to the cc-pV basis sets significantly improved the atomization energy of SO_2 . They suggested that adding two tight d functions to the cc-pV sets would yield an accurate value; in this work we denote such a series of basis sets as cc-pV+2d. More recently Martin¹⁵ showed that the addition of diffuse functions was also required. However Martin did not use two tight d functions, but instead used a series where a tight d was added to aug-cc-pVTZ, a 2d1f set of tight functions was added to aug-cc-pVQZ, and a 3d2f1g set was added to the aug-cc-pV5Z set; we denote this series as aug-cc-pV+d,2df,3d2fg. Using this series of basis sets in conjunction with a variable α extrapolation approach, Martin found excellent agreement with experiment for the atomization energies of SO and SO_2 . The geometries and anharmonic force fields were also quite accurate. Martin optimized the geometries at the CCSD(T) level, which would be impractical for larger systems using such large basis sets. Martin did not include scalar relativistic effects nor correct the core-valence contribution for basis set superposition error (BSSE). In addition, Martin did not note that other extrapolation approaches did not agree well with the value obtained using the variable α approach.

In our very recent study¹³ of SF_n , we used an aug-cc-pV+d,df,dfg series since this family of basis sets yielded very similar results for two-point n^{-3} , two-point n^{-4} , three-point $n^{-4} + n^{-6}$, and variable α approaches. In addition to a consistent extrapolation, this series yielded an SF_6 atomization energy in good agreement with experiment. This basis set series is similar to the one used by Martin in his SO and

SO₂ study.

In this manuscript we reinvestigate SO and SO₂. We consider different families of basis sets using several different extrapolation techniques. Our goals being to determine if one can judge a family of basis sets to be reliable based on the consistency of the extrapolated results. It is also important to determine if one can find a procedure where only the TZ and QZ results are required for an accurate extrapolation, since the 5Z calculations can become very expensive. That is, can one use only the n^{-3} and n^{-4} extrapolations in conjunction with the TZ and QZ basis sets and be assured that the results are accurate. In addition, we investigate the importance of the BSSE correction for the calculations of the CV effect and the magnitude of the scalar relativistic effect. We also investigate the difference in atomization energy arising from using the CCSD(T) geometry instead of one determined using the DFT geometry. We also report results for SF, SF⁺ and SF₆ to compare the best family of basis sets for two different types of molecules.

II. METHODS

Geometries are optimized using the hybrid¹⁶ B3LYP¹⁷ approach in conjunction with the 6-31+G* basis set¹⁸. The diffuse functions are added to improve the description of the ionic component of the bonding. The harmonic frequencies confirm that the stationary points correspond to minima and are used to compute the zero-point energies.

The orbitals are optimized using the self-consistent-field (SCF) approach. The energetics are computed using second order Møller-Plesset¹⁹ (MP2) or the restricted^{20,21} CCSD(T) approach, RCCSD(T). In the valence MP2 and RCCSD(T) calculations only the S 3s and 3p and the fluorine and oxygen 2s and 2p electrons are correlated. The basis sets are derived from the aug-cc-pV sets⁹⁻¹². As discussed previously, it is necessary to add tight functions to S to obtain a good description of the SF_n and

SO_n species. To account for core-valence (CV) effects, RCCSD(T) calculations are performed in which all electrons, except the S 1s, are correlated. The basis sets need to be modified for the calculation of CV effects. The tight functions and CV modifications are discussed below. The RCCSD(T) calculations are performed using Molpro 96²², while the B3LYP calculations are performed using Gaussian94²³.

To improve the accuracy of the results, several extrapolation techniques are used. We use the two-point n^{-3} scheme described by Helgaker *et al.*⁴. We also use the two-point n^{-4} , three-point ($n^{-4} + n^{-6}$), and variable α ($n^{-\alpha}$) schemes described by Martin⁵. Unfortunately it is not possible to perform the RCCSD(T) calculations in the aug-cc-pVQZ and aug-cc-pV5Z basis sets for very large systems. Therefore it is sometimes necessary to extrapolate the MP2 results to the basis set limit, and the question naturally arises, is the best extrapolation method for the MP2 the same as for the CCSD(T) approach.

The scalar relativistic contribution (+R), the mass-velocity and Darwin terms, is computed using perturbation theory. These calculations use a complete-active-space self-consistent-field/multireference configuration interaction (CASSCF/MRCI) approach. Only the s and p valence electrons are correlated at the MRCI level. The S and O valence p orbitals are in the CASSCF/MRCI active space. Internal contraction (IC) is used to reduce the length of the MRCI expansion. The aug-cc-pVTZ basis set is used in these calculations, but with the s space completely uncontracted; for SO_2 , the +R correction is 0.12 kcal/mol larger if the normal contracted aug-cc-pVTZ set is used. The effect of spin-orbit coupling on the dissociation energy is computed using experiment. For the atoms, we use the difference between the lowest m_j component and the m_j weighted average energy²⁴.

III. RESULTS AND DISCUSSION

A. SO and SO₂

In order to compare our extrapolated valence numbers with experiment, we must make some estimate of the core-valence correlation effects. Our results are summarized in Table I. In 1994, Bauschlicher and Partridge²⁵ computed the core-valence effect on the D_e of N₂. Starting from the cc-pVQZ set, they added one p, two d and two f tight functions. In present study, the same number of tight functions are added, but the cc-pVTZ set is used as the starting point. The s and p spaces are uncontracted. The tight functions are even-tempered with a β of 3.0, but with the exponents rounded to the nearest 0.5, as recommended by Martin¹⁵, and is denoted cc-pVTZ+1p2d2f. The CV effect computed at this level is 0.40 kcal/mol, which is very similar to the value (0.41 kcal/mol) reported by Martin, despite any differences in the geometry. The CV effect is reduced to 0.34 kcal/mol if BSSE is accounted for. Adding the diffuse functions, yielding the aug-pVTZ+1p2d2f set, increases the D_e , but reduces the CV effect.

The next two series of calculations use a somewhat different approach for the core-valence basis set. The sets are derived from the aug-cc-pVTZ and aug-cc-pVQZ sets. The p space is uncontracted, while the s space is recontracted. For the S TZ(QZ) basis, the inner 10(11) s functions are contracted to two using the atomic orbitals, and the remaining functions are uncontracted. For the O TZ(QZ) set, the inner 5(6) s functions are contracted to one function. Since Bauschlicher and Partridge²⁵ found the tight p function to have a very small effect, it is not included. To ensure saturation of the tight d space, three tight d functions ($\beta=2.5$) are added to the S and O basis set. Two tight f ($\beta=3.0$) are also added to S and O. These sets are denoted aug-cc-pVTZ+3d2f and aug-cc-pVQZ+3d2f. The aug-cc-pVTZ+3d2f and aug-cc-pVQZ+3d2f sets yield the same CV effect once BSSE has been accounted

for. These results differ by only 0.02 kcal/mol from that obtained using the aug-cc-pVTZ+1p2d2f set.

The results for SO_2 are given in Table II. The cc-pVTZ+1p3d2f results are taken from Martin¹⁵; note that Martin added a third tight d function using a β of 3.0. The aug-cc-pVTZ+3d2f basis set yields a larger atomization energy, but a smaller CV effect, as found for SO. The aug-cc-pVTZ+3d2f CV value is further reduced if BSSE is accounted for. Thus the SO_2 results are consistent with those found for SO, with our values being slightly smaller than those reported by Martin, as a result of our including the diffuse functions and accounting for BSSE.

The computed dissociation energies of the $X^3\Sigma^-$ state of SO are summarized in Table III as a function of basis set. The cc-pV and aug-cc-pV sets are those given by Dunning and co-workers. The number and type of tight functions added to S are added to the end of the basis set label. The β for these functions is the lesser of 3 and the β determined using the two tightest functions in the original basis set.

An inspection of the results yields several obvious conclusions. The BSSE decreases and the D_e increases as the basis sets are improved from TZ to 5Z. The D_e increases even if the BSSE correction is included. Adding the diffuse functions increases the S(O) BSSE, but decreases the O(S) BSSE; it also increases the D_e values. Adding the tight functions has little effect on the BSSE and increases the D_e . The increase in D_e with the tight functions is very large at the TZ level and drops off quickly with improvement in the basis set, such that the effect of the tight functions is small at the 5Z level. The first d function has the largest effect. The second d has a larger effect than the first tight f function. It should also be noted that much of the effect of the tight functions is observed at the SCF level.

The extrapolated results for the SO D_e are summarized in Table IV. The first line is derived from the results reported by Martin¹⁵ using the aug-cc-pV+d,2df,3d2fg series. We first note the large α and the similar results for the variable α and $n^{-4}+n^{-6}$

extrapolation techniques. The two-point approaches using the TZ and QZ basis sets yield results that are larger than three-point values. The cc-pV results show a large variation with extrapolation approach; correcting for BSSE or adding the diffuse functions does not significantly improve the results. Adding the tight functions significantly improves the agreement between the different extrapolation methods. The aug-cc-pV+d and aug-cc-pV+d,df,dfg results are very similar. The variation with extrapolation technique is very small for the aug-cc-pV+2d and aug-cc-pV+2df sets and even the two-point approaches based on the TZ and QZ sets are in good agreement with the three-point approaches.

Our $n^{-4} + n^{-6}$ and variable α extrapolated aug-cc-pV+2d values are smaller than those obtained by Martin, but most of this difference arises from using the B3LYP/6-31+G* geometry ($r=1.5156 \text{ \AA}$), which is longer than the CCSD(T) optimized values. The final line in Table IV is the aug-cc-pV+2d extrapolation using $r=1.49 \text{ \AA}$, which is close to the average of Martin's aug-cc-pVTZ+d and aug-cc-pVQZ+2df results. At this geometry, the aug-cc-pV+2d three-point extrapolation values are in excellent agreement with Martin, but the agreement of the two-point methods with the three-point methods for the aug-cc-pV+2d series is much better than for the series proposed by Martin.

Martin²⁶ has noted that using a cc-pVTZ+d basis set yields a B3LYP geometry of 1.489 \AA , which is in much better agreement with the CCSD(T) results. This is also true for the SO_2 geometry discussed below. Hence the problem with the B3LYP/6-31+G* geometry appears to be associated with the basis set.

In Table V the extrapolation results for the SO_2 atomization energy are summarized. The results labeled "Martin" are obtained using his results from the aug-cc-pVTZ+d,2df,3d2fg series. For this series, the variable α and $n^{-4} + n^{-6}$ extrapolation techniques yield similar results, but the agreement between these two techniques is not as good as for SO. The difference between the n^{-3} and n^{-4} approaches using the

TZ and QZ basis set and the three-point approaches is rather large. Clearly for this choice of tight functions, the 5Z basis set calculation must be performed.

As found for SO, the cc-pV and aug-cc-pV sets do not yield reliable results for SO₂. There is a wide variation in the result depending on the extrapolation technique. Adding one tight d function improves the agreement between the different extrapolation methods significantly, but the variation is still a few kcal/mol. When the second d function is added, the agreement between all of the methods is good. Of special interest is the accuracy of the two-point extrapolation techniques using the TZ and QZ basis sets. Adding the f function hardly changes the $n^{-4} + n^{-6}$ result or the two-point approaches using the QZ and 5Z basis set. The n^{-3} technique using the TZ and QZ basis sets improves, but the variable α technique and the n^{-4} technique using the TZ and QZ basis sets differ by more with the $n^{-4} + n^{-6}$ result. Overall the aug-cc-pV+2d set appears to be the best set. It is somewhat disappointing that the difference between the two-point methods using the TZ and QZ basis sets is about the same for the aug-cc-pV+d, aug-cc-pV+2d, aug-cc-pV+d,df,dfg, and aug-cc-pV+2d1f basis sets. That is the difference between these two approaches does not indicate a reliable extrapolation using only the TZ and QZ sets. Thus suggesting that to obtain very accurate results, it is very difficult to avoid at least some 5Z calculations.

The last basis set test for SO₂ involves using an atomic natural orbital²⁷ (ANO) contraction of the cc-pV5Z basis set. We contract the ANO set to the same size as the cc-pVTZ, cc-pVQZ, and cc-pV5Z sets. The extrapolations using these ANO contractions are labeled "ANO" in the table. Clearly this is not an improvement over the original cc-pV series. Thus having tighter functions in the primitive set, but contracting to the size of a cc-pVTZ set does not improve the results. This is perhaps not too surprising as most of the effect of the tight d function on the cc-pVTZ set appears at the SCF level.

As for SO, the B3LYP/6-31+G* geometry ($r=1.4656$ Å and $\angle=118.63^\circ$) dif-

fers from the optimized CCSD(T) values reported by Martin. Using $r=1.44$ Å and $\angle=119.17^\circ$, which are close to the average of Martin's aug-cc-pVTZ+d and aug-cc-pVQZ+2df results, increases the aug-cc-pV+2d atomization energy by about 1 kcal/mol. The agreement between the different extrapolation methods is very good, and much better than found by Martin.

In Table VI we summarize our best estimate for the atomization energies of SO and SO₂. Our extrapolated D_e values are taken from the $n^{-4}+n^{-6}$ extrapolation using the aug-pV+2d basis set. We pick these values because this basis set yields the best agreement between the various extrapolation methods and the $n^{-4}+n^{-6}$ extrapolation approach shows the smallest variation for the basis sets with tight functions. We report present work (PW) for both the B3LYP/6-31+G* geometry and the geometry derived from Martin's CCSD(T) results. We first note that our SO extrapolated D_e value for the B3LYP geometry is smaller than Martin's value, but that our value at the CCSD(T) geometry is in very good agreement with Martin. For SO₂ our B3LYP value is in very good agreement with Martin, but our value at the CCSD(T) geometry is 1.3 kcal/mol larger. The effect of spin-orbit is taken from experiment²⁴ and therefore is the same for both geometries and for the work of Martin. The scalar relativistic effect, which is computed at the B3LYP geometry, reduces the atomization energy. The core-valence correction, also computed at the B3LYP geometry, increases the atomization energy. However, as noted above our values are smaller than those of Martin because we have included diffuse functions and accounted for BSSE. Our zero-point energy (ZPE) is taken from Martin, however, using the B3LYP value would not change our results significantly. Our D_0 values computed using the CCSD(T) geometries are in good agreement with experiment²⁸⁻³⁰. Our values computed using the B3LYP/6-31+G* geometry are 0.65 and 1.32 kcal/mol smaller than those using the CCSD(T) geometry.

For SO, our best value is 0.57 kcal/mol smaller than Martin; most (0.48 kcal/mol)

of this difference comes from his neglect of the scalar relativistic effect and overestimation of core-valence correlation. For SO_2 our best value and that of Martin only differ by 0.05 kcal/mol, however, this agreement is fortuitous, as Martin neglected the scalar relativistic effect (-0.81 kcal/mol) and overestimated the core-valence effect by neglecting the BSSE and did not include diffuse functions in the calculation of the CV effect (but did include diffuse functions in the valence treatments). Our best atomization energies for SO and SO_2 suggest that the most reliable extrapolation occurs for the basis set family with the most consistent results for the various extrapolation methods.

B. SF, SF^+ , SF_6

In a recent study¹³ of the thermochemistry of SF_n and its ions, we found, that like SO and SO_2 , it was necessary to add tight functions to the S atom. For these systems we used the series aug-cc-pVTZ+d,df,dfg. This series was picked due to the consistency of the extrapolated results. In this manuscript we report on results for the aug-cc-pV+2d sets that worked the best for SO and SO_2 .

For SF and SF^+ at the CCSD(T) level, the various extrapolation methods agree reasonably well, excluding the aug-cc-pV set, which is missing the tight functions. It would be difficult to pick the best basis set among the aug-cc-pV+d, aug-cc-pV+d,df,dfg, and aug-cc-pV+2d series based only on the agreement between the different extrapolation approaches. The aug-cc-pV+2d results are 0.2-0.3 kcal/mol smaller than the other two series, thus suggesting that even after finding a series that yields similar extrapolation results there is some uncertainty in the results.

The MP2 level extrapolation of SF_6 is given in the bottom of the table. The results are very similar to those given for SF and SF^+ , but the differences are magnified by a much larger atomization energy. The aug-cc-pV results clearly vary too much with extrapolation technique to be reliable. While the aug-cc-pV+2d results show the

smallest difference between the two three-point approaches, the n^{-3} TZ QZ results are 3.08 kcal/mol larger than the $n^{-4} + n^{-6}$ results. The aug-cc-pV+1d and aug-cc-pV+d,df,dfg results are reasonably consistent with each other. As with SF and SF⁺, the α is larger than 4.5 for the aug-cc-pV+2d series. The results are also similar to those found for SO₂ by Martin, where the two three-point approaches agree very well, but differed from the two-point approaches, and the α was larger than 4.5. The origin of the difference between the aug-cc-pV+1d, aug-cc-pV+2d, and aug-cc-pV+d,df,dfg series is not in the description of the correlation energy; for each method, the extrapolated correlation contribution to the atomization energies are very similar for all three series of basis sets; for example the $n^{-4} + n^{-6}$ extrapolation method yields 296.50, 296.37, and 296.57 kcal/mol, for the three series of basis sets. In addition, the correlation contribution is very similar for the different extrapolation methods. The difference between the three basis set families comes at the SCF level, where the aug-cc-pVQZ+2d set yields an atomization energy of 226.86 kcal/mol, which is larger than the aug-cc-pV5Z+2d value of 226.68 kcal/mol. That is, for this series reducing the BSSE is more important than basis set incompleteness for the change from QZ to 5Z, where as for all other basis set improvements, the incompleteness is larger than the BSSE and hence the SCF atomization energy increases with basis set improvement. Extrapolation with BSSE corrected values would probably allow an improved extrapolation, but the 5Z calculations are already very expensive and the need to compute the BSSE just makes the problem worse. A comparison of the various extrapolation techniques appears to detect such problems; perhaps an α larger than 4.5 is another indication of such a problem, but that speculation requires additional testing.

As discussed in detail previously¹³ the aug-cc-pV+d,df,dfg series results in a heat of formation of SF₆ that is in good agreement with experiment. The aug-cc-pV+2d series would reduce the computed value by one kcal/mol, which would improve the

agreement with one experiment but worsen the agreement with the other. Thus, unlike SO and SO₂, it is impossible to use experiment to decide on the best extrapolation approach. It is disappointing, however, that the most consistent results for SF₆ and SO₂ occur for different families of basis sets, but it is encouraging that it is possible to find a basis set series where the extrapolation is consistent for all of the methods, and that the result for the most consistent series is in good agreement with the experiment.

IV. CONCLUSIONS

The extrapolation of the atomization energies to the complete basis set limit has been studied. We have not found a way of confirming an extrapolation is reliable using only TZ and QZ results. However, we have found that by comparing the results of various extrapolation techniques using the TZ, QZ, and 5Z basis set it appear possible to pick the most reliable basis set series. Using the B3LYP/6-31+G* geometry introduces about 0.6 kcal/mol per bond error for SO and SO₂. Accounting for BSSE and adding diffuse functions to the valence basis set reduces the effect of core-valence correlation, but makes the results more consistent for different choices of basis set. The scalar relativistic effects are sufficiently large that they need to be considered for second row atoms if accurate atomization energies are required.

REFERENCES

- ¹ Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.
- ² Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
- ³ Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.
- ⁴ Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639.
- ⁵ Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 669.
- ⁶ Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.
- ⁷ Ricca, A.; Bauschlicher, C. W. *J. Chem. Phys.* **1998**, *102*, 876.
- ⁸ Bauschlicher, C. W.; Partridge, H. *Chem. Phys. Lett.* **1995**, *240*, 533.
- ⁹ Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
- ¹⁰ Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
- ¹¹ Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.
- ¹² Woon, D. E.; Peterson, K. A.; Dunning, T. H., unpublished.
- ¹³ Bauschlicher, C. W.; Ricca, A. *J. Phys. Chem.*, in press.
- ¹⁴ Martin, J. M. L.; Uzan, O. *Chem. Phys. Lett.* **1998**, *282*, 16.
- ¹⁵ Martin, J. M. L. *J. Chem. Phys.* **1998**, *108*, 2791.
- ¹⁶ Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- ¹⁷ Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

- ¹⁸ Frisch, M. J.; Pople, J. A.; Binkley, J. S., *J. Chem. Phys.* **1984**, *80*, 3265 and references therein.
- ¹⁹ Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.
- ²⁰ Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219.
- ²¹ Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.
- ²² MOLPRO 96 is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, and P. R. Taylor. The closed shell CCSD program is described in C. Hampel, K. Peterson, and H.-J. Werner, *Chem. Phys. Lett.* **190**, 1 (1992).
- ²³ Gaussian 94, Revision D.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
- ²⁴ Moore, C. E. Atomic energy levels, Natl. Bur. Stand. (US) circ. **1949**, 467.
- ²⁵ Bauschlicher, C. W.; Partridge, H. *J. Chem. Phys.* **1994**, *100*, 4329.
- ²⁶ Martin, J. M. L., personal communication.
- ²⁷ Almlöf, J.; Taylor, P. R. *J. Chem. Phys.* **1987**, *86*, 4070.
- ²⁸ Huber, K. P.; Herzberg, G. "Constants of Diatomic Molecules", (Van Nostrand Reinhold, New York, 1979).

²⁹ Clerbaux, G.; Colin, R. *J. Mol. Spectrosc.* **1994**, *165*, 334.

³⁰ Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.

TABLES

TABLE I. The effect of core-valence on the dissociation energy of $\text{SO } ^3\Sigma^-$, in kcal/mol.

| | BSSE | | | | D_e | | | |
|----------|--------------------|---------|------|---------|--------------|---------|----------------------|---------|
| | S | | O | | without BSSE | | with BSSE correction | |
| | SCF | CCSD(T) | SCF | CCSD(T) | SCF | CCSD(T) | SCF | CCSD(T) |
| | cc-pVTZ+1p2d2f | | | | | | | |
| valence | 0.04 | 0.78 | 0.23 | 1.13 | 51.74 | 118.78 | 51.47 | 116.88 |
| CV | 0.04 | 0.83 | 0.23 | 1.13 | 51.74 | 119.18 | 51.47 | 117.22 |
| Δ | | | | | | | 0.40 | 0.34 |
| | aug-cc-pVTZ+1p2d2f | | | | | | | |
| valence | 0.06 | 0.97 | 0.13 | 0.43 | 49.89 | 120.45 | 49.70 | 119.05 |
| CV | 0.06 | 1.04 | 0.13 | 0.44 | 49.89 | 120.78 | 49.70 | 119.30 |
| Δ | | | | | | | 0.33 | 0.25 |
| | aug-cc-pVTZ+3d2f | | | | | | | |
| valence | 0.06 | 0.97 | 0.13 | 0.43 | 49.90 | 120.46 | 49.72 | 119.07 |
| CV | 0.06 | 1.05 | 0.13 | 0.44 | 49.90 | 120.81 | 49.72 | 119.32 |
| Δ | | | | | | | 0.35 | 0.27 |
| | aug-cc-pVQZ+3d2f | | | | | | | |
| valence | 0.01 | 0.33 | 0.05 | 0.24 | 50.17 | 122.90 | 50.11 | 122.32 |
| CV | 0.01 | 0.63 | 0.05 | 0.25 | 50.17 | 123.47 | 50.11 | 122.59 |
| Δ | | | | | | | 0.57 | 0.27 |

TABLE II. The effect of core-valence on the atomization energy of SO₂, in kcal/mol.

| | BSSE | | | | D_e | | | |
|----------|------|---------|------|-----------------------------|--------------|---------|----------------------|---------|
| | S | | O | | without BSSE | | with BSSE correction | |
| | SCF | CCSD(T) | SCF | CCSD(T) | SCF | CCSD(T) | SCF | CCSD(T) |
| | | | | cc-pVTZ+1p3d2f ^a | | | | |
| valence | | | | | | 245.99 | | |
| CV | | | | | | 246.76 | | |
| Δ | | | | | | 0.77 | | |
| | | | | aug-cc-pVTZ+3d2f | | | | |
| valence | 0.13 | 2.66 | 0.38 | 1.38 | 115.55 | 248.85 | 115.04 | 244.81 |
| CV | 0.13 | 2.85 | 0.38 | 1.40 | 115.55 | 249.58 | 115.04 | 245.33 |
| Δ | | | | | | 0.73 | | 0.52 |

^a From Martin¹⁵.

TABLE III. The dissociation energy of $\text{SO } ^3\Sigma^-$, in kcal/mol.

| | BSSE | | | | D_e | | | |
|-----------------|------|------------------|------|------|---------|--------|-----------|--------|
| | S | | O | | no BSSE | | with BSSE | |
| | SCF | (T) ^a | SCF | (T) | SCF | (T) | SCF | (T) |
| cc-pVTZ | 0.04 | 0.71 | 0.21 | 1.21 | 45.54 | 114.35 | 45.29 | 112.42 |
| cc-pVQZ | 0.01 | 0.27 | 0.07 | 0.49 | 48.08 | 120.02 | 48.01 | 119.26 |
| cc-pV5Z | 0.00 | 0.18 | 0.01 | 0.17 | 49.68 | 123.02 | 49.67 | 122.67 |
| aug-cc-pVTZ | 0.06 | 1.02 | 0.12 | 0.64 | 46.65 | 116.96 | 46.47 | 115.30 |
| aug-cc-pVQZ | 0.01 | 0.37 | 0.05 | 0.34 | 48.46 | 121.32 | 48.41 | 120.61 |
| aug-cc-pV5Z | 0.00 | 0.22 | 0.01 | 0.12 | 49.82 | 123.59 | 49.81 | 123.26 |
| aug-cc-pVTZ+d | 0.06 | 1.04 | 0.12 | 0.65 | 48.92 | 119.07 | 48.74 | 117.37 |
| aug-cc-pVTZ+2d | 0.06 | 1.04 | 0.12 | 0.66 | 49.50 | 119.59 | 49.32 | 117.90 |
| aug-cc-pVTZ+2df | 0.06 | 1.01 | 0.13 | 0.67 | 49.75 | 119.99 | 49.56 | 118.31 |
| aug-cc-pVQZ+d | 0.01 | 0.36 | 0.05 | 0.34 | 49.72 | 122.47 | 49.66 | 121.76 |
| aug-cc-pVQZ+2d | 0.01 | 0.36 | 0.05 | 0.34 | 50.09 | 122.81 | 50.03 | 122.11 |
| aug-cc-pVQZ+df | 0.01 | 0.35 | 0.05 | 0.35 | 49.74 | 122.50 | 49.68 | 121.80 |
| aug-cc-pVQZ+2df | 0.01 | 0.35 | 0.05 | 0.35 | 50.11 | 122.85 | 50.05 | 122.15 |
| aug-cc-pV5Z+d | 0.00 | 0.21 | 0.01 | 0.12 | 50.16 | 123.90 | 50.15 | 123.57 |
| aug-cc-pV5Z+2d | 0.00 | 0.21 | 0.01 | 0.12 | 50.20 | 123.94 | 50.19 | 123.61 |
| aug-cc-pV5Z+2df | 0.00 | 0.21 | 0.01 | 0.12 | 50.20 | 123.96 | 50.19 | 123.63 |
| aug-cc-pV5Z+dfg | 0.00 | 0.21 | 0.01 | 0.12 | 50.16 | 123.94 | 50.15 | 123.61 |

^a Signifies CCSD(T).

TABLE IV. Extrapolation of SO dissociation energy, in kcal/mol.

| basis ^b | Method ^a | | | | | |
|---------------------|---------------------|--------|--------|--------|----------|---------------|
| | 3 | 3 | 4 | 4 | 4+6 | α^c |
| | TZ,QZ | QZ,5Z | TZ,QZ | QZ,5Z | TZ,QZ,5Z | TZ,QZ,5Z |
| Martin ^d | 126.78 | 126.07 | 126.12 | 125.78 | 125.67 | 125.60(4.615) |
| cc-pV | 124.16 | 126.17 | 123.30 | 125.46 | 126.22 | 129.86(1.813) |
| cc-pV-BSSE | 124.24 | 126.24 | 123.20 | 125.43 | 126.22 | 129.32(2.063) |
| aug-cc-pV | 124.50 | 125.98 | 123.84 | 125.44 | 126.01 | 128.58(1.872) |
| aug-cc-pV-BSSE | 124.49 | 126.04 | 123.68 | 125.41 | 126.02 | 128.41(2.068) |
| aug-cc-pV+d | 124.95 | 125.41 | 124.43 | 125.07 | 125.30 | 125.83(2.778) |
| aug-cc-pV+d-BSSE | 124.97 | 125.47 | 124.30 | 125.04 | 125.31 | 125.88(2.892) |
| aug-cc-pV+2d | 125.16 | 125.12 | 124.67 | 124.86 | 124.92 | 125.01(3.585) |
| aug-cc-pV+2d-BSSE | 125.18 | 125.19 | 124.54 | 124.83 | 124.93 | 125.08(3.511) |
| aug-cc-pV+2df | 124.93 | 125.13 | 124.50 | 124.87 | 125.00 | 125.24(3.128) |
| aug-cc-pV+2df-BSSE | 124.94 | 125.19 | 124.36 | 124.84 | 125.01 | 125.31(3.155) |
| aug-cc-pV+d,df,dfg | 125.01 | 125.44 | 124.48 | 125.10 | 125.32 | 125.82(2.829) |
| | At $r=1.49$ Å | | | | | |
| aug-cc-pV+2d | 125.80 | 125.77 | 125.28 | 125.49 | 125.57 | 125.67(3.559) |

^a The value of signifies the type extrapolation, for example “3” indicates an n^{-3} extrapolation, “4+6” indicates an $n^{-4} + n^{-6}$ extrapolation, and “ α ” indicates the variable extrapolation. The second line shows which basis sets are used in the extrapolation.

^b The basis sets are described in detail in the text.

^c The α is given in parentheses.

^d At the CCSD(T) optimized distance using the aug-pV+d,2df,3d2fg set¹⁵.

TABLE V. Extrapolation of SO₂ atomization energy, in kcal/mol.

| basis ^b | Method ^a | | | | | |
|---------------------|---|--------|--------|--------|----------|---------------|
| | 3 | 3 | 4 | 4 | 4+6 | α^c |
| | TZ,QZ | QZ,5Z | TZ,QZ | QZ,5Z | TZ,QZ,5Z | TZ,QZ,5Z |
| Martin ^d | 262.34 | 259.93 | 260.70 | 259.30 | 258.81 | 258.64(5.085) |
| cc-pV | 256.45 | 262.41 | 254.34 | 260.55 | 262.74 | 276.32(1.510) |
| aug-cc-pV | 257.10 | 262.09 | 255.34 | 260.54 | 262.37 | 273.78(1.507) |
| aug-cc-pV+d | 258.37 | 260.12 | 257.17 | 259.25 | 259.98 | 262.26(2.377) |
| aug-cc-pV+2d | 259.16 | 259.12 | 258.05 | 258.51 | 258.67 | 258.88(3.559) |
| aug-cc-pV+2df | 258.62 | 259.13 | 257.65 | 258.53 | 258.84 | 259.44(3.071) |
| aug-cc-pV+d,df,dfg | 258.60 | 260.18 | 257.38 | 259.32 | 260.01 | 261.99(2.484) |
| ANO | 255.28 | 261.19 | 253.51 | 259.52 | 261.64 | 278.93(1.229) |
| | At $r=1.44$ Å and $\angle=119.17^\circ$ | | | | | |
| aug-cc-pV+2d | 260.49 | 260.46 | 259.32 | 259.82 | 259.99 | 260.24(3.541) |

^a The value of α signifies the type extrapolation, for example “3” indicates an n^{-3} extrapolation, “4+6” indicates an $n^{-4} + n^{-6}$ extrapolation, and “ α ” indicates the variable extrapolation. The second line shows which basis sets are used in the extrapolation.

^b The basis sets are described in detail in the text.

^c The α is given in parentheses.

^d At the CCSD(T) optimized distance using the aug-pV+d,2df,3d2fg set¹⁵.

TABLE VI. Best estimate for the dissociation energy, kcal/mol.

| | SO | | | SO ₂ | | |
|---------------------|----------------------|----------------------|---------|----------------------|---------|---------|
| | PW | | Martin | PW | | Martin |
| Geometry | B3LYP | CCSD(T) | CCSD(T) | B3LYP | CCSD(T) | CCSD(T) |
| Extrapolated D_e | 124.92 | 125.57 | 125.62 | 258.67 | 259.99 | 258.64 |
| Spin-orbit | -0.78 | -0.78 | -0.78 | -1.01 | -1.01 | -1.01 |
| Scalar relativistic | -0.34 | -0.34 | | -0.81 | -0.81 | |
| Core-valence | 0.27 | 0.27 | 0.41 | 0.52 | 0.52 | 0.77 |
| Best D_e | 124.03 | 124.68 | 125.25 | 257.13 | 258.69 | 258.40 |
| Zpt ^a | 1.64 | 1.64 | 1.64 | 4.38 | 4.38 | 4.38 |
| D_0 | 122.39 | 123.04 | 123.61 | 252.75 | 254.07 | 254.02 |
| Experimental D_0 | 123.58 ²⁸ | 123.24 ²⁹ | | 253.97 ³⁰ | | |

^a The zero-point energy is taken from Martin¹⁵. The B3LYP values for SO and SO₂ are 1.60 and 4.22 kcal/mol, respectively.

TABLE VII. Extrapolation of atomization energies, in kcal/mol.

| basis ^b | Method ^a | | | | | |
|--------------------|---------------------|--------|--------|--------|----------|---------------|
| | 3 | 3 | 4 | 4 | 4+6 | α^c |
| | TZ,QZ | QZ,5Z | TZ,QZ | QZ,5Z | TZ,QZ,5Z | TZ,QZ,5Z |
| | CCSD(T) | | | | | |
| SF | | | | | | |
| aug-cc-pV | 84.34 | 84.74 | 83.88 | 84.44 | 84.63 | 85.08(2.808) |
| aug-cc-pV+d | 84.69 | 84.44 | 84.27 | 84.24 | 84.23 | 84.22(4.088) |
| aug-cc-pV+2d | 84.76 | 84.31 | 84.37 | 84.14 | 84.06 | 84.02(4.698) |
| aug-cc-pV+d,df,dfg | 84.76 | 84.46 | 84.34 | 84.27 | 84.24 | 84.22(4.195) |
| SF ⁺ | | | | | | |
| aug-cc-pV | 87.86 | 88.69 | 87.24 | 88.25 | 88.61 | 89.66(2.461) |
| aug-cc-pV+d | 88.39 | 88.21 | 87.85 | 87.94 | 87.97 | 88.00(3.828) |
| aug-cc-pV+2d | 88.52 | 88.00 | 88.01 | 87.78 | 87.70 | 87.65(4.555) |
| aug-cc-pV+d,df,dfg | 88.50 | 88.24 | 87.95 | 87.97 | 87.98 | 87.98(3.961) |
| | MP2 | | | | | |
| SF ₆ | | | | | | |
| aug-cc-pV | 522.56 | 527.89 | 519.91 | 525.80 | 527.88 | 536.41(2.004) |
| aug-cc-pV+d | 524.62 | 525.01 | 522.79 | 523.96 | 524.37 | 525.02(3.331) |
| aug-cc-pV+2d | 525.61 | 523.59 | 523.94 | 522.90 | 522.53 | 522.35(4.773) |
| aug-cc-pV+d,df,dfg | 524.86 | 525.08 | 523.01 | 524.04 | 524.40 | 524.94(3.414) |

^a The value of signifies the type extrapolation, for example "3" indicates an n^{-3} extrapolation, "4+6" indicates an $n^{-4} + n^{-6}$ extrapolation, and " α " indicates the variable extrapolation. The second line shows which basis sets are used in the extrapolation.

^b The basis sets are described in detail in the text.

^c The optimized α value is given in parentheses.